1,042,639

PATENT SPECIFICATION

NO DRAWINGS

1,042,639

Date of Application and filing Complete Specification: Aug. 4, 1964.
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COMPLETE SPECIFICATION

Substituted Phenols

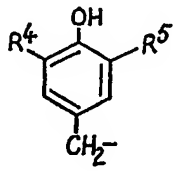
We, UNITED STATES RUBBER COMPANY, of Rockefeller Centre, 1230 Avenue of the Americas, New York 100—20, State of New York, United States of America, a corporation organized and existing under the laws of the State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods of making chemical compounds containing a hydroxydialkylbenzyl group and to certain new hydroxydialkylbenzyl compounds, the term "alkyl" including cycloalkyl and aralkyl.

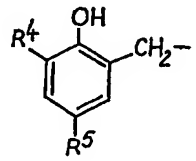
The compounds made according to the present invention are useful as antioxidants.

This invention consists in a method of making a compound of the formula A_2S, AOR, ASR^1, A_2NR^2, ANR^2R^3 or A—S—X—S—A; wherein:—

A represents


I

or


II

R^4 and R^5 being the same or different and representing alkyl, cycloalkyl or aralkyl groups having up to 12 carbon atoms,

R represents an alkyl, cycloalkyl, aralkyl or hydroxyalkyl group having up to 12 carbon atoms,

R^1 represents an alkyl, hydroxyalkyl, aryl, cycloalkyl or aralkyl group having up to 18 carbon atoms,

R^2 and R^3 may be the same or different and represent H, OH or an alkyl, cycloalkyl, hydroxyalkyl, aralkyl or aryl group having up to 12 carbon atoms, or NR^6R^7,

R^6 and R^7 being the same or different and representing hydrogen or alkyl, cycloalkyl, aralkyl or aryl groups having up to 12 carbon atoms,

and X represents a diradical containing from 2 to 18 carbon atoms,

which method comprises treating a compound having the formula AZ, wherein A has the above significance, and

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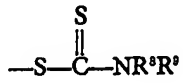
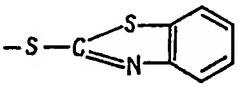
Z represents



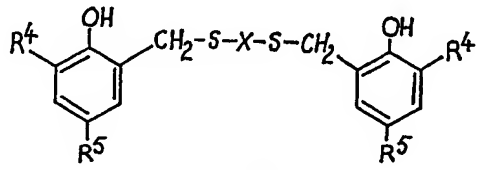
R^8 and R^9 being the same or different and representing lower alkyl groups, or, in the case where A has formula II above, Z may alternatively represent



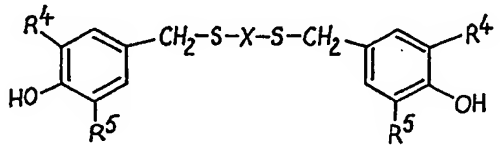
with an alkali metal sulfide, or with an alkali metal hydroxide and an active hydrogen containing compound having the formula ROH, R^1SH, NH_2R^2 or NHR^2A, NHR^2R^3 or H—S—X—S—H, wherein

R, R^1, R^2, A, R^3 and X have the above significance, the reaction being effected in an inert solvent, or when ROH is used, in an excess of ROH, and isolating the resulting compound of the formula A_2S, AOR, ASR^1, A_2NR^2, ANR^2R^3 or A—S—X—S—A.

This invention further consists in a compound having the formula



or



wherein R^4 and R^5 may be the same or different and represent alkyl, cycloalkyl or aralkyl groups having up to 12 carbon atoms and X is a diradical containing from 2 to 18 carbon atoms.

The term "lower alkyl group", when used in this specification, means an alkyl group having from one to five carbon atoms.

It is preferred that the solvent should be a water-miscible solvent for instance an aliphatic alcohol, dioxan or ethylene glycol dimethyl ether. Alternatively the reaction may be effected in a mixture of water and an aromatic hydrocarbon, for instance benzene or xylene.

The reaction is preferably effected at a temperature between 20° C. and 100° C., more preferably between 50° C. and 100° C. Generally the reaction is effected under reflux at the boiling point of the solvent.

The preferred reaction time is up to about 2 hours. Longer times may be used but they are not necessary as the reaction is generally complete in 30 minutes or less. The preferred pH of the reaction system is about 8.5.

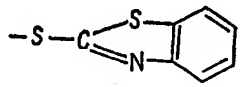
Examples of R^4 and R^5 in the radical A are methyl, ethyl, isopropyl, *tert.*butyl, *tert.*octyl, decyl, dodecyl, *cyclo*hexyl, *cyclo*heptyl, *cyclo*octyl, benzyl, α-methyl benzyl and α,α-dimethyl benzyl radicals.

The intermediate compounds AZ wherein Z is may be prepared from the corresponding 2,4- or 2,6-dialkyl phenol (referred to as A^1H in the following equation), formaldehyde, carbon disulfide and the corresponding dialkylamine according to the method described in U.S. Patent No. 2,757,174 and as illustrated by the following equation:

$$HCHO + A^1H + CS_2 + NHR^8R^9 \rightarrow A{-}S{-}\overset{\overset{S}{\|}}{C}{-}NR^8R^9 + H_2O$$

The groups R^8 and R^9 are preferably alkyl groups having up to 6 carbon atoms each, for instance, methyl, ethyl, *iso*propyl, butyl or amyl groups, since the alkali metal dithiocarbamates having these groups are sufficiently water-soluble to facilitate working up and avoid contamination of the product.

The intermediates AZ wherein Z is the



group may be prepared by reacting the corresponding dialkyl phenol with formaldehyde and mercaptobenzothiozole under acid conditions in a reaction similar to that described in United States Patents Nos. 2,134,957 and 2,150,463.

Examples of suitable dialkyl phenols are 2,4-dimethyl phenol, 2-methyl-4-*tert.*-butyl phenol, 2-*tert.*butyl-4-methyl phenol, 2,4-di-*tert.*butyl phenol, 2-methyl-4-*cyclo*hexyl phenol, 2-*cyclo*hexyl-4-methyl phenol, 2,4-di-*cyclo*hexyl phenol, 2-methyl-4-*tert.*octyl phenol, 2-*tert.*octyl-4-methyl phenol, 2,4-di-*tert.*octyl phenol, 2-nonyl-4-methyl phenol, 2-methyl-4-nonyl phenol, 2,4-dinonyl phenol, 2-methyl-4-(α-methyl benzyl) phenol, 2-(α-methyl benzyl)-4-methyl phenol, 2,4-di-(α-methylbenzyl) phenol, 2-methyl-4-(α,α-dimethylbenzyl) phenol, 2-(α,α-dimethylbenzyl)-4-methyl phenol, 2,4-di(α,α-dimethylbenzyl) phenol, 2,6-di-*tert.*butyl phenol, 2,6-xylenol, 2-methyl-6-*tert.*-butyl phenol, 2,6-di-*iso*propyl phenol, 2-methyl-6-*cyclo*hexyl phenol, 2-methyl-6-*tert.*-octyl phenol, 2,6-di-*tert.*octyl phenol, 2-methyl-6-(α-methyl benzyl) phenol and 2-methyl-6-(α,α-dimethyl benzyl) phenol.

Compounds of the formula A_2S

One mole of the compound AZ is preferably reacted with approximately 0.5 mole of alkali metal sulfide. If less than 0.5 mole equivalent of the alkali metal sulfide is used the reaction will be incomplete and the product will contain unreacted starting material. If more than 0.5 mole or equivalent of the alkali metal sulfide is used reaction will be complete but recovery of the carbon disulfide and the amine from the by-product dialkyl dithiocarbamate will be complicated by the presence of excess metal sulfide. For these reasons the use of about 0.5 mole or equivalent of the alkali metal sulfide is preferred. The equation for the reaction is as follows:

$$2AZ + Na_2S \rightarrow 2NaZ + A_2S$$

It should be noted that an alkali metal hydrosulfide such as NaSH may be used in combination with an equimolar amount of alkali metal hydroxide such as NaOH as the precursor or source of the alkali metal sulfide such as Na_2S.

Compounds of the formula A—S—X—S—A

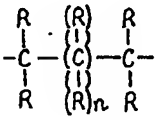
Two moles of AZ are preferably reacted with at least two moles of alkali metal hydroxide and one mole of H—S—X—S—H. The reaction may be represented as follows:

$$2AZ + 2NaOH + H{-}S{-}X{-}S{-}H \rightarrow 2NaZ + 2H_2O + A{-}S{-}X{-}S{-}A.$$

The diradical X may be aliphatic or may contain cyclo aliphatic or aromatic groups. The diradical may contain in addition hetero atoms such as sulphur, oxygen or nitrogen. Thus, for example, X may be

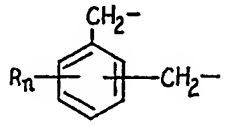
(a) A polymethylene diradical of the formula $-(CH_2)_n-$ wherein n is a whole number from 2 to 12, for example $-CH_2CH_2-$ and $-(CH_2)_{12}-$.

(b) A branched chain polyalkylene diradical of the formula:

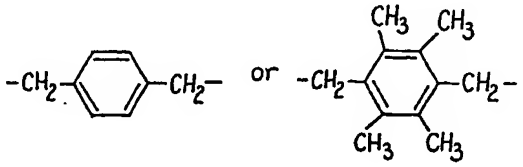


wherein n is a whole number from 0 to 9 and the R groups may be hydrogen or alkyl groups and a least one of the R groups is an alkyl group, for example —CH_2—$CH(CH_3)$— and —CH_2—$C(CH_3)_2$—CH_2—.

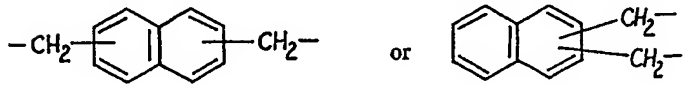
(c) An aralkyl diradical of the formula:



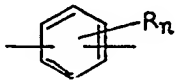
wherein R is an alkyl group of 1 to 4 carbon atoms and n is a whole number from 0 to 4, for example:



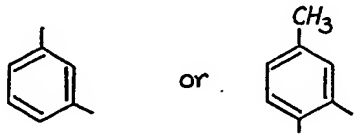
(d) An aralkyl diradical of the formula:



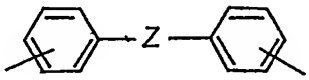
(e) An aromatic diradical of the formula:



wherein R is an alkyl radical and n is a whole number from 0 to 4, for example:

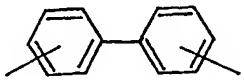


(f) An aromatic diradical of the formula:

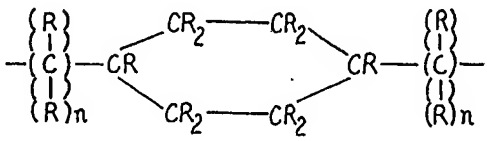


wherein Z is —O—, —S— or —SO_2—.

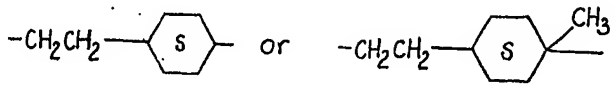
(g) An aromatic diradical of the formula:



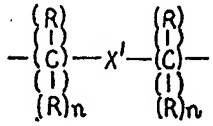
(h) A cyclic hydrocarbon containing diradical of the general formula:



wherein R may be hydrogen or an alkyl group and n is a whole number from 0 to 6, for example:



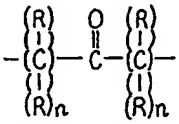
(i) An aliphatic diradical, containing hetero atoms, of the general formula:



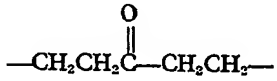
wherein R may be hydrogen or alkyl, n is a whole number from 1 to 6 and X′ is —O—, —S—, —SO_2— or —NR′— (wherein R′ is an alkyl group), for example: —$CH_2CH_2OCH_2CH_2$—, —$CH_2CH_2SCH_2CH_2$— or —$CH_2CH_2SO_2CH_2CH_2$—.

(j) A diradical of the formula:
—$CH_2CH_2OCH_2CH_2OCH_2CH_2$— or —$CH_2CH_2OCH_2OCH_2CH_2$—

(k) A diradical of the formula:



wherein R may be hydrogen or alkyl and n is a whole number from 1 to 5, for example:



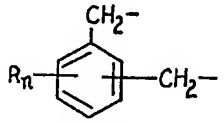
Suitable dimercaptans (dithiols) of the formula H—S—X—SH include the following:

(a) 1,2-ethanedithiol
1,4-butanedithiol
1,10-decanedithiol
(b) 2,2-dimethyl-1,3-propanedithiol
(c) α,α′-dimercapto-p-xylene
bis(mercaptomethyl) durene
(d) bis(mercaptomethyl)naphthalene
(e) toluenedithiol
(f) p,p′-oxybis(thiophenol)
(4,4′-dimercaptodiphenyl ether)
(g) dimercapto diphenyl
(h) 2-mercaptoethyl-4-mercaptocyclohexane
(i) β,β′-dimercaptodiethyl ether
β,β′-dimercaptodiethyl sulfide
β,β′-dimercaptodiethyl methylamine
(j) 1,2-bis(β-mercaptoethoxy)ethane
(k) β,β′-dimercaptodiethyl ketone

Particularly preferred products of the invention are those derived from dimercaptans of the formula H—S—X—S—H in which X is as defined previously and is

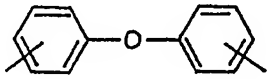
(I) a polymethylene diradical of the formula $-(CH_2)_n-$ wherein n is a whole number from 2 to 12,

(II) an aralkyl diradical of the formula:

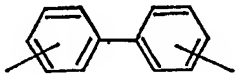


wherein R is an alkyl group of 1 to 4 carbon atoms and n is a whole number from 0 to 4

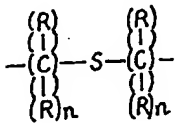
(III) an aromatic diradical of the formula:



(IV) an aromatic diradical of the formula:

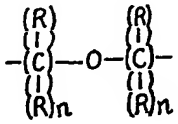


(V) an aliphatic diradical of the formula:



wherein R is hydrogen or alkyl (e.g., 1—4 carbon atoms) and n is a whole number from 0 to 6, or

(VI) an aliphatic diradical of the general formula:



wherein R is hydrogen or alkyl (e.g., 1—4 carbon atoms) and n is a whole number from 0 to 6.

The compounds of the formula AS—X—SA are novel. Preferred products (i.e., those resulting from combination of the described preferred phenolic intermediate compounds and the described preferred dimercaptans) include bis (2-hydroxy-3-alkyl-5-alkyl benzylthio) alkanes, bis(2-hydroxy-3-alkyl-5-alkyl benzylthio)alkylbenzenes (also called α,α'-bis(2-hydroxy-3-alkyl-5-alkylbenzylthio)-dialkyl benzenes), bis(2 - hydroxy - 3 - alkyl - 5 - alkyl benzylthio) dialkyl ethers, bis(2 - hydroxy - 3-aralkyl - 5 - alkyl benzylthio) alkylbenzenes (also called α,α' - bis (2 - hydroxy-3 - aralkyl - 5 - alkylbenzylthio) dialkylbenzenes), bis(2 - hydroxy - 3 - alkyl - 5-alkylbenzylthio) - diphenyl ethers, bis(2 - hydroxy - 3 - alkyl - 5 - alkylbenzylthio)-alkyl cyclohexanes, bis(2 - hydroxy - 3 - alkyl - 5 - alkylbenzylthio) dialkyl sulfides (especially diethyl sulfides), bis(2-hydroxy-3-alkyl-5-alkylbenzylthio) biphenyls, in which the alkyl and aralkyl groups contain up to 12 carbon atoms, bis(3-alkyl-4-hydroxy-5-alkyl benzylthio)-alkanes, bis(3-alkyl-4-hydroxy-5-alkyl benzylthio)-alkylbenzenes, bis(3-alkyl-4-hydroxy-5-alkyl benzylthio)dialkyl ethers, α,α'bis(3-alkyl-4-hydroxy-5-alkyl benzylthio)-dialkylbenzenes, bis(3-alkyl-4-hydroxy-5-alkylbenzylthio)-

dialkyl sulfides, bis(3-alkyl-4-hydroxy-5-alkylbenzylthio)biphenyl, and bis(3-alkyl-4-hydroxy-5-alkyl benzylthio) diphenyl ethers, in which the alkyl groups contain up to 12 carbon atoms.

Those compounds of the formula AS—X—SA in which A has the formula II above may also be prepared by a direct reaction of a 2,4-dihydrocarbyl phenol with formaldehyde and a dimercaptan under acid catalysis. A preparation of this type is described in Example No. 17 below. However, the process of the present invention gives a much purer product.

Compounds of the formula ASR'

Preferably one mole of AZ is reacted with one mole of R'SH and at least one mole of alkali metal hydroxide. The reaction is illustrated by the following equation:

$$AZ + R'SH + NaOH \rightarrow ASR' + NaZ + H_2O.$$

The mercaptans which may be used are primary, secondary and tertiary mercaptans having from 1 to 18, preferably from 1 to 12, carbon atoms; and include methyl mercaptan, *tert*dodecyl mercaptan, octadecyl mercaptan, hydroxy alkyl mercaptans, such as mercapto ethanol, *cyclo*alkyl mercaptans, such as *cyclo*hexyl mercaptan and terpene mercaptans, aryl mercaptans such as thiophenol and substituted thiophenols (e.g. *p*-tert butyl thiophenol, aralkyl mercaptans, such as benzyl mercaptan.

Compounds of the formula A—O—R

Preferably one mole of AZ is reacted with at least one mole of alkali metal hydroxide and at least one mole of ROH. The reaction is illustrated by the following equation:

$$AZ + ROH + NaOH \rightarrow AOR + NaZ + H_2O$$

Conveniently the reaction is effected in excess of ROH which acts as a solvent.

The alcohol ROH may be methanol, ethanol, *iso*propanol, butanol, cyclohexanol, benzyl alcohol or dodecanol.

Compounds of the formula ANR^2R^3 and A_2NR^2

The compounds ANR^2R^3 are preferably prepared by reacting one mole of AZ with at least one mole of an alkali metal hydroxide and at least one mole of R^2R^3NH. The equation is as follows:

$$AZ + NaOH + R^2R^3NH \rightarrow ANR^2R^3 + H_2O + NaZ$$

The compounds A_2NR^2 may be formed by reacting one mole of AZ with at least one mole of an alkali metal hydroxide and at least one mole of $ANHR^2$. The equation is as follows:

$$AZ + ANHR^2 + NaOH \rightarrow A_2NR^2 + NaZ + H_2O$$

They may also be formed by reacting one mole of AZ with at least one mole of alkali metal hydroxide and half a mole of R^2NH_2 according to the following equation:

$$2AZ + NH_2R^2 + 2NaOH \rightarrow A_2NR^2 + 2H_2O + 2NaZ$$

Suitable amines which may be used are:

1. ammonia
2. primary and secondary alkyl amines from methyl- and dimethylamine to dodecyl- and didodecyl amine.
3. *cyclo*alkylamines such as cyclohexyl amine and dicyclohexyl amine
4. aralkylamines such as benzylamine and dibenzylamine
5. aromatic amines such as aniline, N-methylaniline, p-diphenylamine and phenyl-β-naphthylamine
6. hydroxyalkyl amines such as ethanolamine and diethanolamine
7. hydroxylamine

The present invention is illustrated by the following Examples:

EXAMPLE No. 1.

Preparation of bis(3-methyl-4-hydroxy-5-t-butylbenzyl) sulfide.

354 lbs. of a 42.6 aqueous solution of sodium dimethyldithiocarbamate, 164 lbs. of 2-methyl-6-t-butylphenol, 97 lbs. of methanol as solvent and 80 lbs. of 37%

aqueous formaldehyde were charged with agitation to a 100 gallon glass lined reactor. Over a period of 30 minutes, 53 lbs. of 66° Be' sulfuric acid were added while the temperature of the mixture was held below 35° C. The mixture was then refluxed for 2—1/2 hours, cooled to 50° C., and the solid portion was allowed to crystallize. The mother liquor was removed through a filter stick at 50° C. and the solid (3-methyl-5-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate) was washed with two 50 gallon portions of 50° C. water.

Methanol (97 lbs.) was then added to the solid and, after 5 minutes of agitation, a solution of 60 lbs. of 60% sodium sulfide and 40 lbs. of water was charged to the reactor. The reaction mixture was heated to reflux for 30 minutes and then cooled to 30° C. The product was separated by filtration, washed first with a solution of 70 lbs. of water and 30 lbs. of methanol and then with hot water, and dried. The yield of bis(3-methyl-4-hydroxy-5-t-butylbenzyl) sulfide was 181 lbs. (94% yield), m.pt. = 115.5°—118° C.

EXAMPLE No. 2.

Preparation of bis(3,5-dimethyl-4-hydroxybenzyl) sulfide.

2,6-Di-t-butylphenol (103 g., 0.5 mole), 37% aqueous formaldehyde (40.5 g., 0.5 mole), 25% aqueous dimethylamine (90 g., 0.5 mole), carbon disulfide (40 g., 0.52 mole) and 400 ml. of ethanol were mixed and heated under reflux for 1—1/2 hours. The precipitate which formed was separated by filtration and washed with ethanol, yielding 152 g. (90% yield) of 3,5-di-t-butyl-4-hydroxybenzyl-N,N-dimethyldithiocarbamate.

A portion of the intermediate thus obtained weighing 17 g. (0.05 mole) was added to a solution of 12 g. (0.05 mole) of $Na_2S.9H_2O$ in 10 ml. of water and 50 ml. of methanol. The mixture was heated to reflux and a heavy slurry of a white precipitate formed. The slurry was cooled and diluted with 100 ml. of water. The product was then separated by filtration and dried, yielding 11.5 g. (98% yield) of bis(3,5-di-t-butyl-4-hydroxybenzyl) sulfide, m.pt. = 141°—142° C.

EXAMPLE No. 3.

Preparation of bis(3,5-dimethyl-4-hydroxybenzyl) sulfide.

A mixture of 244 g. (2 moles) of 2,6-xylenol, 162 g. (2 moles) of 37% aqueous formaldehyde, 360 g. (2 moles) of 25% aqueous dimethylamine and 160 g. (2.1 moles) of carbon disulfide in 400 ml. of methanol was stirred and refluxed for 2 hours. The mixture formed 2 layers and, after cooling and stirring, the lower layer crystallized. The product was separated by filtration and dried, yielding 467 g. (90% yield) of 3,5-dimethyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate.

A portion of the intermediate thus obtained (127 g., 0.5 mole) was dissolved in 350 ml. of methanol by heating at 50° C. A solution of 66 g. (0.275 mole) of $Na_2S.9H_2O$ in 50 ml. of water was then added and the mixture was refluxed for 15 minutes. The solution was then cooled and diluted with 350 ml. of water. The white precipitate which formed was separated by filtration, washed with water and dried, yielding 70 g. (90% yield) of bis(3,5-dimethyl-4-hydroxybenzyl)sulfide, m.pt. = 97°—99° C.

EXAMPLE No. 4.

Preparation of bis(2-hydroxy-3-t-butyl-5-methylbenzyl)sulfide.

2-Hydroxy-3-t-butyl-5-methylbenzyl N,N-dimethyldithiocarbamate was first prepared in the following manner:

A solution of 328 g. (2 moles) of 2-t-butyl-p-cresol, 178 g. (2.2 moles) of 37% aqueous formaldehyde and 396 g. (2.2 moles) of 25% aqueous dimethylamine in 900 ml. of methanol was heated slowly during two hours to reflux and then was refluxed for one hour. The product separated as an oil which crystallized when the reaction mixture was cooled with stirring. The crystalline product was filtered off, washed with aqueous methanol and dried. The weight of 2-t-butyl-4-methyl-6-dimethylaminomethyl phenol formed was 398 g. (90%), m.p. 49—51° C.

A portion of the Mannich base weighing 22 g. (0.1 mole) and 8 g. (0.1 mole) of carbon disulfide were dissolved in 40 ml. of ethylene glycol monoethyl ether and heated at reflux for 20 hours. The pot temperature rose from 97° to 118° C. during this time. The solution was cooled and the product precipitated by dilution of the solution with water. It was filtered off and dried yielding 16 g. (55%) of 2-hydroxy-3-t-butyl-5-methylbenzyl N,N-dimethyldithiocarbamate, m.p. 97—98° C.

A solution of 12 g. (0.05 mole) of $Na_2S.9H_2O$ in 150 ml. of ethanol was added to a reactor charged with 29.7 g. (0.1 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl N,N-dimethyldithiocarbamate. The mixture was heated to reflux for 20 minutes,

diluted with water and cooled. The product was separated by filtration, washed and dried. The yield of bis(2-hydroxy-3-t-butyl-5-methylbenzyl) sulfide was 83%.

EXAMPLE No. 5.

Preparation of bis (2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl) sulfide.

A solution of 110 g. (0.5 mole) of 2-(1,1,3,3-tetramethylbutyl)-p-cresol, 100 g. (1.25 Mole) of 37% aqueous formaldehyde and 112 g. (0.5 mole) of 25% aqueous dimethylamine in 350 ml. of methanol was heated at reflux for two hours. The solution was then cooled in an ice bath and the white, crystalline product was separated by filtration and dried. The weight of the 2-(1,1,3,3-tetramethylbutyl)-4-methyl-6-dimethylaminomethylphenol was 126 g. (91% yield), m.pt. = 43°—48° C.

A portion of the latter compound weighing 83 g. (0.3 mole) and 24 g. (0.3 mole) of carbon disulfide were combined with 100 ml. of ethylene glycol monoethyl ether and heated at reflux for seven hours. The solution was then cooled and poured into water. The product separated as an oil and then crystallized. It was dried and recrystallized from hexane. The yield of 2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl N,N-dimethyldithiocarbamate was 44 g. (41% yield), m.pt. = 105°—107° C.

A solution of 35.3 g. (0.1 mole) of the latter compound and 12 g. (0.05 mole) of $Na_2S.9H_2O$ in 250 ml. of 80% aqueous ethanol was heated at reflux for ten minutes. The hot solution was filtered and cooled. The precipitate which crystallized out was separated by filtration and washed with 80% aqueous ethanol. The yield of bis(2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl)sulfide was 21.5 g. (87% yield), m.pt. = 90°—92° C.

EXAMPLE No. 6.

Preparation of bis(2-hydroxy-3-(alpha,alpha-dimethyl-benzyl)-5-methylbenzyl)-sulfide.

A solution of 7.2 g. (0.02 mole) of 2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl N,N-dimethyldithiocarbamate (prepared in 47% yield from the reaction of 2-(alpha,alpha-dimethylbenzyl)-4-methyl-6-dimethylaminomethyl phenol with carbon disulfide) and 2.4 g. (0.01 mole) of $Na_2S.9H_2O$ in 25 ml. of ethanol was heated at reflux for 30 minutes. The hot solution was filtered and cooled. The precipitate which crystallized out was separated by filtration, washed with ethanol and dried. The yield of bis(2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl)-sulfide was 3.5 g. (70% yield), m.pt. = 113°—114° C.

EXAMPLE No. 7.

Using the procedure of Examples 2 and 3, the following compounds were also prepared:

bis(3,5-dicyclohexyl-4-hydroxybenzyl)sulfide (76% yield, m.pt. = 128°—132° C.); and bis(3,5-diisopropyl-4-hydroxybenzyl)sulfide (93% yield, m.pt. = 92° C.).

EXAMPLE No. 8.

Preparation of bis(2-hydroxy-3-t-butyl-5-methylbenzyl) sulfide.

The intermediate 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide was prepared in the following manner:

2-Mercaptobenzothiazole (584.5 g., 3.5 moles) was suspended in one liter of isopropyl alcohol in a 3-liter, 3-neck flask equipped with a mechanical stirrer, condenser, thermometer and additional funnel. To the suspension was added 292 g. (3.6 moles) of 37% aqueous formaldehyde and the mixture was warmed to 60—70° C. for 30 minutes. 2-t-Butyl-p-cresol (492 g., 3 moles) was then added followed by 100 ml. of concentrated hydrochloric acid. The mixture was then refluxed for four hours with stirring, the crystalline product beginning to precipitate out after one hour. The mixture was cooled and the product was filtered off, washed with isopropyl alcohol and dried. The yield of 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide was 744 g. (yield 72%), m.p. 164—165° C.

A solution of 128.8 g. (0.375 mole) of the 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide and 48 g. (0.2 mole) of $Na_2S.9H_2O$ in 150 ml. of ethanol was heated under reflux for one hour. The solution was then diluted with water until slightly cloudy. On cooling, a solid precipitate formed. The mixture was diluted further with 100 ml. of water slowly with stirring. The precipitate was then filtered off, washed with 50% aqueous ethanol and dried. The yield of bis(2-hydroxy-3-t-butyl-5-methylbenzyl) sulfide was 68 g. (94%), m.p. 77—80° C. Analysis: Calculated—% C, 74.6; % H, 8.87; % S, 8.28. Found: % C, 74.84; % H, 8.66; % S, 8.09.

EXAMPLE NO. 9.

Preparation of bis(2-hydroxy-3-(1,1,3,3-tetramethylbutyl-5-methylbenzyl)sulfide.

The intermediate 2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl 2-benzothiazolyl sulfide was prepared in the following manner:

A mixture of 1100 g. (5 moles) of 2-(1,1,3,3-tetramethylbutyl)-p-cresol, 162 g. (5 moles) of paraformaldehyde, 835 g. (5 moles) of 2-mercaptobenzothiazole, 10 g. of p-toluenesulfonic acid and 1500 ml. of benzene was placed in a 5-liter, 3-neck flask equipped with stirrer, thermometer, Stark and Dean trap and condenser. The mixture was heated to reflux (80° C.) for six hours, during which time the water of reaction was azeotroped out and collected. A total of 90 ml. of water was collected (quantitative). The benzene was then distilled off, the last part in vacuo. The solid residue weighed 2,017 g. (quantitative) and was recrystallized from ethanol. The yield of recrystallized 2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl 2-benzothiazolyl sulfide was 1,660 g. (yield 83%), m.p. 101—103° C.

A solution of 16 g. (0.04 mole) of the 2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl 2-benzothiazolyl sulfide and 4.8 g. (0.02 mole) of $Na_2S.9H_2O$ in 25 ml. of ethanol was heated on the steam bath for 30 minutes. The solution was poured into water and the product was extracted with hexane. The hexane solution was evaporated to an oil which was crystallized from methanol to yield 7 g. (70%) of bis(2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl)sulfide, m.p. 92—93° C.

EXAMPLE NO. 10.

Preparation of bis(2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl)-sulfide.

The intermediate 2-hydroxy-3-(alpha,alphadimethylbenzyl)-5-methylbenzyl 2-benzothiazolyl sulfide was prepared in the following manner:

A mixture of 226 g. (1 mole) of 2-(alpha,alphadimethylbenzyl)-p-cresol, 33 g. (1.1 mole) of paraformaldehyde, 167 g. (1 mole) of 2-mercaptobenzothiazole, 2g. of p-toluene-sulfonic acid and 250 ml. of benzene was placed in a one-liter, 3-neck flask and refluxed for four hours. The water of reaction (16 ml.) was azeotroped out as formed and collected in a Stark and Dean trap (theory = 18 ml.). The benzene solution was washed with dilute aqueous sodium hydroxide to remove unreacted 2-mercapto-benzothiazole and was then concentrated down to a liquid residue which was crystallized from benzene. The yield of 2-hydroxy-3-(alpha,alphadimethylbenzyl)-5-methylbenzyl 2-benzothiazolyl sulfide was 101.5 g. (yield 33%), m.p. 141—143° C.

A solution of 81.2 g. (0.2 mole) of 2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl benzothiazolyl sulfide and 24 g. (0.1 mole) of $Na_2S.9H_2O$ in 250 ml. of ethanol was heated on the steam bath for 1—1/2 hours. The solution was cooled and the crystalline product was filtered off, washed with ethanol and dried. The yield of bis(2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl)sulfide was 40.5 g. (80%), m.p. 114—115° C.

EXAMPLE NO. 11.

Preparation of 1,2-bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)-ethane.

A solution of 7 g. (0.11 mole) of potassium hydroxide (85% active) in 20 ml. of water was added to a solution of 4.7 g. (0.05 mole) of 1,2-ethanedithiol in 100 ml. of ethanol. 2-Hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide (34.3 g., 0.1 mole) was then added and the mixture was heated to near reflux for 15 minutes. The solution was then cooled and the crystalline product which precipitated was filtered off, washed with cold ethanol and dried. The yield of 1,2-bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)ethane was 19 g. (85%), m.pt. 95—96° C.

Analysis: Calc'd. — % S = 14.35.
Found — % S = 14.39, 14.53

EXAMPLE NO. 12.

Preparation of alpha,alpha'-bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)-p-xylene.

A solution of 6.6 g. (0.1 mole) of potassium hydroxide (85% active) in 10 ml. of water was added to 50 ml. of ethylene glycol dimethyl ether containing 8.5 g. (0.05 mole) of alpha,alpha'-dimercapto-p-xylene. 2-Hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide (34.3 g., 0.1 mole) was then added and the solution was heated at reflux for one hour. The solution was then poured into water and the oily organic product was extracted with ether. The ether extract was washed with water and evaporated down to a liquid residue which crystallized, wt. = 25.5 g. (98%). The

alpha,alpha'-bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)-p-xylene was purified by recrystallization from ethanol giving 19 g. (73%) of white crystals, m.p. 109—111° C.

Analysis: Calc'd. — % S = 12.27.
Found — % S = 12.34, 12.17.

EXAMPLE No. 13.

Preparation of beta,beta'-bis(2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzylthio)diethyl ether.

A solution of 7 g. (0.11 mole) of potassium hydroxide (85% active) in 10 ml. of water was added to 50 ml. of ethanol containing 7 g. (0.05 mole) of beta,beta'-dimercaptodiethyl ether. This solution was then added to 200 ml. of hot ethanol containing 40 g. (0.1 mole) of 2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl 2-benzothiazolyl sulfide. The solution was heated on a steam bath for 10 minutes and then cooled. The product crystallized out and was filtered off, washed with ethanol and dried, m.p. 99—101° C., wt. 24.8 g. (82%).

Analysis: Calc'd. — % S = 10.62.
Found — % S = 10.47, 10.63.

EXAMPLE No. 14.

Preparation of alpha,alpha'-bis(2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzylthio)-p-xylene.

81.2 g. (0.2 mole) of 2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl 2-benzothiazolyl sulfide was reacted with 15 g. (0.22 mole) of 85% KOH (in 20 ml. of water) and 17.2 g. (0.1 mole) of alpha,alpha'-dimercapto-p-xylene in 100 ml. of ethylene glycol dimethyl ether. The product, isolated in 77% yield, had a melting point of 120—121° C.

EXAMPLE No. 15.

Use of a dithiocarbamylmethyl substituted phenol intermediate. Preparation of beta,beta'-bis(2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzylthio)diethyl ether.

A mixture of 35.3 g. (0.1 mole) of 2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl N,N-dimethyl-dithiocarbamate, 6.9 g. (0.05 mole) beta,beta'-dimercaptodiethyl ether, 17.5 ml. (0.1 mole) 6N. NaOH and 60 ml. of ethylene glycol dimethyl ether was heated under reflux for 10 minutes. The solution was then poured into 200 ml. of cold water. The product separated as an oil which gradually became crystalline. The precipitate was filtered off, washed with water and dried, wt. = 25 g. (83%), m.pt. 98—100° C. after recrystallization from hexane.

EXAMPLE No. 16.

Preparation of beta,beta'-bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)diethyl ether.

A mixture of 34.3 g. (0.1 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide, 6.9 g. (0.05 mole) of beta,beta'-dimercaptodiethyl ether and 150 ml. of ethanol was placed in a 500 ml. 3-neck flask fitted with a stirrer, thermometer and condenser. A solution of 4.4 g. (0.11 mole) of sodium hydroxide in 20 ml. of water was then added and the mixture was heated to reflux for 60 minutes. The solution was then poured into 500 ml. of water and the organic product which separated was extracted with hexane-ether. The extract was washed with water, dried with anhyd. potassium carbonate and evaporated to an oil which crystallized. The beta,beta'-bis-(2-hydroxy-3-t-butyl-5-methylbenzylthio)diethyl ether obtained weighed 24.5 g. (quantitative), m.p. 62—64° C. after recrystallization from hexane.

EXAMPLE No. 17.

Preparation of beta,beta'-bis(2-hydroxy-3-nonyl-5-methylbenzylthio)diethyl ether.

A mixture of 93.6 g. (0.4 mole) of 2-nonyl-p-cresol, 13 g. (0.4 mole) of paraformaldehyde, 27.6 g. (0.2 mole) of beta,beta'-dimercaptodiethyl ether, 1 g. of p-toluene sulfonic acid and 100 ml. of benzene was placed in a 500 ml. 3-neck flask fitted with a thermometer, stirrer and Stark and Dean trap with condenser. The solution was then heated to reflux and the water formed in the reaction (7 ml.) was collected in the Stark and Dean trap. The reaction was complete in about two hours. The benzene solution was then diluted with hexane, washed with aqueous sodium bicarbonate and water, and dried with anhydrous potassium carbonate. The solution was then evaporated down on a steam bath. The beta,beta'-bis(2-hydroxy-3-nonyl-5-

methylbenzylthio)-diethyl ether was obtained as a viscous liquid weighing 123 g. (97%).

EXAMPLE No. 18.

Preparation of p,p'-bis(2-hydroxy-3-t-butyl-5-methyl-benzylthio)diphenyl ether.

p,p'-Dimercaptodiphenyl ether (11.7 g., 0.05 mole) was dissolved in a solution of 6.6 g. (0.1 mole) of 85% potassium hydroxide in 20 ml. of 50% aqueous ethanol. This was then added to a mixture of 32.2 g. (0.094 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolylsulfide in 500 ml. of ethanol and the solution was heated at reflux for 30 minutes. The solution was then cooled and diluted with 100 ml. of water.

The precipitate which separated was filtered off and dried. The p,p'-bis(2-hydroxy-3-t-butyl-5-methylbenzylthio) diphenyl ether obtained weighed 24.5 g. (90%), m.p. 158—160° C. after recrystallization from ethanol.

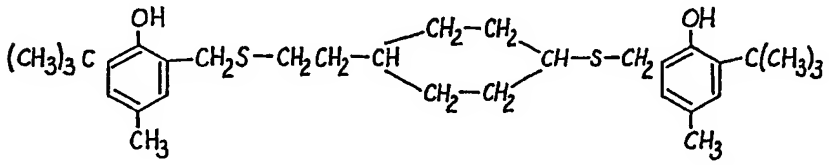
EXAMPLE No. 19.

Preparation of beta(2-hydroxy-3-t-butyl-5-methylbenzylthio)ethyl-4-(2-hydroxy-3-t-butyl-5-methylbenzylthio) cyclohexane.

A solution of 68.6 g. (0.2 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide, 17.6 g. (0.1 mole) of beta-mercaptoethyl-4-mercaptocyclohexane, 13.2 g. (0.2 mole) of 85% potassium hydroxide in 20 ml. of water and 200 ml. of ethylene glycol dimethyl ether was heated at reflux for one hour. Some of the solvent (150 ml.) was then distilled out. The mother liquor was poured into ice water. The viscous liquid product which separated was extracted with hexane, washed with water and dried with anhyd. potassium carbonate. The hexane solution was then evaporated down and the product was obtained as a viscous liquid.

Analysis: Calc'd. — % S = 12.10
Found — % S = 11.94

Formula:



EXAMPLE No. 20.

Preparation of beta,beta'-bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)diethyl sulfide.

2-Hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide (34.3 g., 0.1 mole) was reacted with 7.7 g. (0.05 mole) of beta,beta'-dimercaptodiethyl sulfide and 4.4 g. (0.11 mole) of sodium hydroxide in 20 ml. of water and 150 ml. of ethanol in the same way as described above for dimercaptodiethyl ether (example 16). The product was obtained as a viscous liquid in 85% yield.

EXAMPLE No. 21.

Preparation of p,p'-bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)biphenyl.

To a solution of 2.2 g. (0.01 mole) of p,p'-dimercaptobiphenyl and 1.4 g. (0.02 mole) of 85% potassium hydroxide in 10 ml. of water and 30 ml. of ethanol was added 6.9 g. (0.02 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide. The mixture was heated on the steam bath for two hours. It was then poured into water and the product extracted was ether. Evaporation of the ether extract gave the product as a solid residue, m.p. 145—147° C. after recrystallization from hexane.

EXAMPLE No. 22.

This example demonstrates the usefulness of the compounds of this invention as antioxidants for rubber. Films prepared from a butadiene-styrene carboxylated latex and containing two parts of the antioxidant per 100 parts of rubber were placed in a 270° F. oven and observed for signs of resinification.

Antioxidant	Time to Resinify, Hours
(1) None	10
(2) 2-t-butyl-4-methyl-6-(beta-hydroxyethylthiomethyl)-phenol	44
(3) 2-octyl-4-methyl-6-(beta-hydroxy-ethylthiomethyl) phenol	72
(4) beta, beta'-bis (2-hydroxy-3-t-butyl-5-methylbenzylthio)-diethyl ether	587
(5) beta, beta'-bis (2-hydroxy-3-octyl-5-methylbenzylthio)-diethyl ether	683

EXAMPLE No. 23.

This example demonstrates the usefulness of the compounds of this invention as antioxidants for polyurethane foams. The compounds are effective in preventing the discoloration of the foam due to heat or light as demonstrated in the following tests.

(a) Heat aging.

Slices of a polyester based polyurethane foam containing 2 parts of the antioxidant per 100 parts of foam were placed in a circulating air oven at 290° F. for 17 hours. (Suitable foam may be prepared, for example in accordance with R. J. Ferrari et al., Ind. Eng. Chem., *50*, 1041 (1958), type A in Table I. The ingredients except toluene diisocyanate, may be mixed at slow speed for 90 seconds in a wax container. The mixture may be allowed to stand for 90 seconds. The toluene diisocyanate may then be added and the formulation mixed at high speed for 20 seconds. The mixture may be poured into a metal mould and allowed to blow. It may then be cured at 100° C. for 15 minutes. The stabilizer to be tested may be dissolved or dispersed in a portion of the polyester.) The samples were then removed and the color of the samples observed.

Antioxidant	Colour Rating
(1) None	cream
(2) beta,beta'-bis (2-hydroxy-3-nonyl-5-methylbenzylthio) diethyl ether	light cream
(3) beta,beta'-bis (2-hydroxy-3-t-butyl-5-methylbenzylthio) diethyl ether	off white

(b) Light aging.

Foam slices were aged for various periods at room temperature on a bench top. During the aging periods, the specimens were exposed to diffuse, indirect sunlight and to direct fluorescent light. The samples were observed for the development of color.

Antioxidant	Colour Rating		
	Initial	3 weeks	6 weeks
(1) None	white	Lt. yellow	yellow
(2) beta,beta'-bis (2-hydroxy-3-nonyl-5-methylbenzylthio) diethyl ether	off white	cream	Lt. yellow
(3) beta,beta'-bis (2-hydroxy-3-t-butyl-5-methylbenzylthio) diethyl ether	white	off white	Lt. cream

EXAMPLE NO. 24.

Preparation of 1,2-bis-(3,5-di-t-butyl-4-hydroxybenzylthio)ethane.

A solution of 95 g. (0.28 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate, 13 g. (0.14 mole) of 1,2-ethanedithiol and 47 ml. (0.28 mole) of 6 N. NaOH in 400 ml. of ethanol was stirred and heated under reflux for ten minutes. A precipitate formed and the solution was cooled and filtered. The product was washed with ethanol and dried yielding 67 g. (90%) of 1,2-bis(3,5-di-t-butyl-4-hydroxybenzylthio)ethane, m.pt. 142—143° C.

Analysis: Calc'd. — % S = 12.05.
Found — % S = 12.36, 12.25.

EXAMPLE NO. 25.

Preparation of alpha,alpha' - bis(3 - methyl - 4 - hydroxy - 5 - t - butylbenzylthio)-p-xylene.

A solution of 17 g. (0.1 mole) of alpha,alpha'-dimercapto-p-xylene, 15 g. (0.22 mole) of potassium hydroxide (85% active) and 20 ml. of water in 300 ml. of methanol was placed in a 500 ml. Erlenmeyer flask. To this solution was added 59.4 g. (0.2 mole) of 3-methyl-4-hydroxy-5-t-butyl-benzyl N,N-dimethyldithiocarbamate and the mixture was heated on the steam bath for about one hour. The mixture was then cooled and the precipitate was filtered off, washed with methanol and dried yielding 46 g. (88%) of alpha,alpha'-bis(3-methyl-4-hydroxy-5-t-butylbenzylthio)-p-xylene, m.pt. 141—142° C.

Analysis: Calc'd. — % S = 12.27.
Found — % S = 12.40, 11.74.

EXAMPLE NO. 26.

Preparation of 1,4-bis(3-methyl-4-hydroxy-5-t-butyl-benzylthio) butane.

3 - Methyl - 4 - hydroxy - 5 - t - butylbenzyl N,N - dimethyldithiocarbamate (45 g., 0.15 mole), 9.1 g. (0.075 mole) of 1,4-dimercaptobutane, 25 ml. (0.15 mole) of 6 N. sodium hydroxide and 50 ml. of ethylene glycol dimethyl ether were mixed and heated under reflux for ten minutes. The clear solution was then cooled and poured into cold water. The product separated as an oil and shortly solidified. The yield of white crystals was 35 g. (98%), m.pt. 96—98° C. after recrystallization from hexane.

Analysis: Calc'd. — % S = 13.50.
Found — % S = 13.60, 13.76.

EXAMPLE NO. 27.

Preparation of beta,beta'-bis(3,5-di-t-butyl-4-hydroxy-benzylthio)diethyl ether.

3,5-Di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate (34 g., 0.1 mole), beta,beta'-dimercaptodiethyl ether (6.9 g., 0.05 mole), 6 N. sodium hydroxide (17.5 ml., 0.1 mole) and ethylene glycol dimethyl ether (40 ml.) were mixed and heated

under reflux for 10 minutes. A clear solution formed and was cooled and poured into 200 ml. of ice water. The product oiled out and then solidified. It was filtered off and washed with 50% aqueous ethanol. The yield of the white solid product was 29 g. (100%). A portion recrystallized from hexane had m.pt. = 89—92° C.

Analysis: Calc'd. — % S = 11.15.
Found — % S = 11.08, 11.29.

EXAMPLE No. 28.

Preparation of 4,4'-bis(3,5-di-t-butyl-4-hydroxybenzylthio)diphenyl ether.

Thirty-four grams (0.1 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate, 11.7 g. (0.05 mole) 4,4'-dimercaptodiphenyl ether, 17 ml. (0.1 mole) 6 N. sodium hydroxide solution and 100 ml. of ethanol were mixed and refluxed for 15 minutes. During reaction a precipitate formed. The mixture was cooled and the product was filtered off, washed with ethanol-water (2:1) and dried. The yield of 4.4'-bis(3,5-di-t-butyl-4-hydroxybenzylthio)diphenyl ether was 26 g. (80%), m.pt. = 126—128° C. after recrystallization from benzene.

EXAMPLE No. 29.

Preparation of 3,4-bis(3,5-di-t-butyl-4-hydroxybenzylthio) toluene.

To a solution of 6.5 g. (0.042 mole) of toluene-3,4-dithiol and 7 g. (0.1 mole) of 85% potassium hydroxide in 10 ml. of water and 100 ml. of ethanol was added 28.2 g. (0.084 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate. The solution was heated at reflux for 15 minutes. It was then poured into water and the organic product was extracted with hexane-ether. The extract was dried with anhydrous potassium carbonate and evaporated on the steam bath. The yield of 3,4-bis(3,5-di-t-butyl-4-hydroxybenzylthio)toluene was 24 g. (96%), m.pt. 114—117° C. after recrystallization from hexane.

EXAMPLE No. 30.

Preparation of alpha,alpha'-bis(3,5-di-t-butyl-4-hydroxybenzylthio)-p-xylene.

A solution of 8.5 g. (0.05 mole) of alpha,alpha'-dimercapto-p-xylene and 8 g. (0.1 mole) of 50% sodium hydroxide in 50 ml. of ethanol was added to a slurry of 33.9 g. (0.1 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate in 200 ml. of hot ethanol. The mixture was heated at reflux for 15 minutes. It was then cooled and the crystalline product was filtered off, washed with ethanol and dried. The yield of alpha,alpha'-bis(3,5-di-t-butyl-4-hydroxybenzylthio)-p-xylene was 28 g. (93%), m.pt. 181—183° C.

EXAMPLE No. 31.

Preparation of beta,beta'-bis(3,5-di-t-butyl-4-hydroxybenzylthio)diethyl sulfide.

A solution of 34 g. (0.1 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate, 7.7 g. (0.05 mole) of beta,beta'-dimercaptodiethyl sulfide and 17.5 ml. (0.1 mole) of 6 N. sodium hydroxide in 40 ml. of ethylene glycol dimethyl ether was heated at reflux for ten minutes. The solution was cooled and poured into 200 ml. of ice water. The product separated as an oil and was extracted with 100 ml. of benzene. The benzene extract was washed with water and the benzene was evaporated off on the steam bath. The residual oil was dried further in a vacuum oven at 80° C. to give the product as a viscous oil. The yield of beta,beta'-bis(3,5-di-t-butyl-4-hydroxybenzylthio)diethyl sulfide was 29.5 g. (99%).

Analysis: Calc'd. — % S = 16.3
Found — % S = 16.9

EXAMPLE No. 32.

Preparation of p,p'-bis(3,5-di-t-butyl-4-hydroxy-benzylthio)biphenyl.

To a solution of 2.2 g. (0.01 mole) of p,p'-dimercaptobiphenyl and 1.6 g. (0.02 mole) of 50% sodium hydroxide in 50 ml. of ethanol was added 6.8 g. (0.02 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate. The solution was heated at reflux for 30 minutes. It was then cooled and the precipitated product was filtered off, washed with ethanol and dried. The yield of p,p'-bis(3,5-di-t-butyl-4-hydroxybenzylthio) biphenyl was 3.7 g. (56%), m.p. 200—205° C.

EXAMPLE No. 33.

Preparation of beta,beta'-bis(3-methyl-4-hydroxy-5-t-butylbenzylthio)diethyl ether.

A solution of 297 g. (1 mole) of 3-methyl-4-hydroxy-5-t-butylbenzyl N,N-dimethyldithiocarbamate, 69 g. (0.5 mole) of beta,beta'-dimercaptodiethyl ether and 170 ml. (1 mole) of 6 N. sodium hydroxide in 360 ml. of ethylene glycol dimethyl ether was heated at reflux for 10 minutes. The solution was cooled and diluted with 500 ml. of water. The oil which separated was extracted with a mixture of 500 ml. of hexane and 100 ml. of benzene. The extract was washed with water, dried with anhydrous sodium sulfate, and evaporated on the steam bath to the product, a viscous oil. The yield of beta,beta'-bis(3-methyl-4-hydroxy-5-t-butylbenzylthio)diethyl ether was 244 g. (quantitative).

EXAMPLE No. 34.

This example demonstrates the usefulness of the compounds of this invention as antioxidants for rubber. Films prepared from a butadiene-styrene carboxylated latex and containing two parts of the antioxidant per 100 parts of rubber were placed in a 270° F. oven and observed for signs of resinification.

Antioxidant	Time to Resinify, hours
(1) none	10
(2) 2-methyl-4-(benzylthio-methyl)-6-t-butylphenol	44
(3) 2,6-di-t-butyl-4-(beta-hydroxyethylthiomethyl)-phenol	44
(4) beta,beta'-bis (3,5-di-t-butyl-4-hydroxybenzylthio)-diethyl ether	995
(5) alpha, alpha'-bis (3-methyl-4-hydroxy-5-t-butylbenzyl-thio)-p-xylene	995

EXAMPLE No. 35.

This example demonstrates the usefulness of the compounds of the invention as stabilizers in polypropylene. In the method used to evaluate the compounds of this invention, 90 mil thick films of the polymer containing 0.3% of the antioxidant and 0.3% of dilauryl thiodipropionate were aged in a circulating air oven maintained at 300° F. The degradation of the polymer sample is readily evident in crazing on the surface or discoloration and crumbling of the edges, the first sign of which is considered to be the break point. Polypropylene containing 0.3% of dilauryl thiodipropionate alone degraded in 12 days.

Antioxidant	Days to degrade
(1) 1,2-bis(3,5-di-t-butyl-4-hydroxybenzylthio)ethane	53
(2) beta,beta'-bis(3,5-di-t-butyl-4-hydroxybenzylthio)diethyl ether	56
(3) alpha,alpha'-bis((3-methyl-4-hydroxy-5-t-butylbenzylthio)-p-xylene	62
(4) alpha-alpha'-bis(3,5-di-t-butyl-4-hydroxybenzylthio)-p-xylene	67

EXAMPLE No. 36.

A natural rubber composition was prepared in accordance with the following recipe:

Masterbatch No. 1	
Pale Crepe	98.65
Zinc Oxide (XX72)	10.00
Lithopone	60.00
Finely divided $CaCO_3$ (whiting)	60.00
Zinc laurate (Laurex (Trade Mark))	0.50
Sulfur	3.00
Masterbatch No. 2	1.50
	233.65

Masterbatch No. 2	
Pale Crepe	90.0
Tetramethylthiuram monosulfide (Monex (Trade Mark))	10.0
	100.0

The antioxidants (1 part) were then milled into 233.65 parts of masterbatch No. 1 and samples were cured at 274° F. for 30 minutes. Tensile bars were aged in an oxygen bomb for 96 hours at 70° C. The percent retention of tensile strength after aging demonstrates the activity of the compounds as rubber antioxidants.

Compound	% Tensile Retained
Blank	0
beta,beta'-bis (3-methyl-4-hydroxy-5-t-butyl-benzylthio)-diethyl ether	43
beta, beta'-bis(3,5-di-t-butyl-4-hydroxybenzylthio)diethyl sulfide	55

EXAMPLE No. 37.

This example demonstrates the usefulness of the compounds of the invention as fat antioxidants using the Schaal oven aging test. Prime steam pork fat, 150 g., was melted and 15 mg. of the chemical mixed in. A peroxide number by the potassium iodide-starch method was then taken as the zero reading. The samples were placed in a 60° C. oven and readings were taken after 3 days and then at one or two week intervals. A peroxide number of 30 is considered to be failure.

Compound	Days to Failure
Blank	7
beta, beta'-bis (3,5-di-t-butyl-4-hydroxybenzylthio) diethyl ether	48—63
beta, beta'-bis (3-methyl-4-hydroxy-5-t-butylbenzylthio) diethyl ether	63
alpha, alpha'-bis (3-methyl-4-hydroxy-5-t-butylbenzylthio)-p-xylene	63

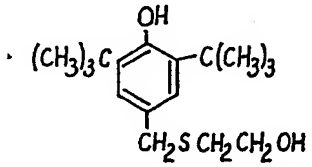
EXAMPLE No. 38.

Preparation of 2,6-di-t-butyl-4-(beta-hydroxyethylthiomethyl)phenol.

A mixture of 33.9 g. (0.1 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate, 7 g. (0.1 mole) of 85% KOH (in 10 ml. of water) and 8 g. (0.1 mole) of beta-mercaptoethanol (RSH where R is $HOCH_2CH_2$—) in 100 ml. of ethanol was heated on the steam bath at reflux temperature until solution was complete (about ten minutes). The solution was then allowed to stand and cool for 30 minutes. It was then poured into 300 ml. of water and the product which separated was extracted with hexane-ether, dried with anhyd. K_2CO_3 and evaporated to a liquid residue which crystallized, wt. = 30 g. (97%), m.p. 55—58° C. The m.p. after one recrystallization from hexane was 58—59° C.

Analysis: Calc'd. — % S, 10.80
Found — % S, 10.48

Formula:

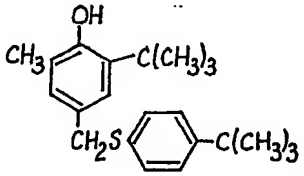


EXAMPLE No. 39.

Preparation of 2-Methyl-4-(p-t-butylphenylthiomethyl)-6-t-butylphenol.

A mixture of 29.7 g. (0.1 mole) of 3-methyl-4-hydroxy-5-t-butylbenzyl N,N-dimethyldithiocarbamate, 7 g. (0.1 mole) of 85% KOH (in 10 ml. of water) and 16.6 g. (0.1 mole) of p-t-butylphenol in 100 ml. of ethanol was heated to near reflux for 10 minutes. The solution was then allowed to cool. It was poured into water and the product was extracted with hexane-ether. The extract was dried with anhyd. K_2CO_3 and evaporated to a liquid product which crystallized, wt. = 33 g. (97%), m.p. 88—89° C. after recrystallization from hexane.

Formula:



EXAMPLE No. 40.

The preparation of 2-t-butyl-4-methyl-6-(p-t-butylphenylthiomethyl)phenol.

To a solution of 3.3 g. (0.02 mole) p-t-butylthiophenol and 1.6 g. (0.02 mole) 50% sodium hydroxide in 25 ml. of ethanol was added 5.9 g. (0.02 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl N,N-dimethyldithiocarbamate. The solution was heated at reflux for 30 minutes and then poured into cold water. The product was extracted with ether and the ether extract was washed with water, dried over anhydrous sodium sulfate and evaporated down to a liquid residue which slowly crystallized. The yield of 2-t-butyl-4-methyl-6-(p-t-butylphenylthiomethyl)phenol was 6 g. (88%), m.p. 49—50° C. after recrystallization from hexane.

In a similar manner, the following chemicals, for example, may be prepared:

2,6-dimethyl-4-(methylthiomethyl)phenol
2,6-diisopropyl-4-(dodecylthiomethyl)phenol
2,6-di-t-butyl-4-(cyclohexylthiomethyl)phenol
2-methyl-4-(dodecylthiomethyl)-6-(alpha-methylbenzyl)phenol
2-methyl-4-(beta-hydroxyethylthiomethyl)-6-(alpha-methylbenzyl)phenol
2-methyl-4-(cyclohexylthiomethyl)-6-(alpha-methylbenzyl)phenol
2,6-di-(alpha-methylbenzyl)-4-(phenylthiomethyl)phenol
2-methyl-4-(ethylthiomethyl)-6-cyclohexylphenol
2,6-dicyclohexyl-4-(phenylthiomethyl)phenol

2,6-di-t-butyl-4-(benzylthiomethyl)phenol
2-methyl-4-(benzylthiomethyl)-6-(alpha-methylbenzyl)phenol
2,4-dimethyl-6-(methylthiomethyl)phenol
2,4-dimethyl-6-(dodecylthiomethyl)phenol
2,4-di-t-butyl-6-(cyclohexylthiomethyl)phenol
2-(dodecylthiomethyl)-4-methyl-6-(alpha-methylbenzyl)phenol
2-(beta-hydroxyethylthiomethyl)-4-methyl-6-(alpha,alpha-dimethylbenzyl)phenol
2-(cyclohexylthiomethyl)-4-methyl-6-(alpha,alpha-dimethylbenzyl)phenol
2-(phenylthiomethyl)-4,6-di-(alpha-methylbenzyl)phenol
2-(ethylthiomethyl)-4-methyl-6-cyclohexylphenol
2,4-di-t-butyl-6-(benzylthiomethyl)phenol

EXAMPLE No. 41.

Preparation of 2-t-butyl-4-methyl-6-(p-t-butyl-phenylthiomethyl)phenol.

To a solution of 16.6 g. (0.1 mole) of p-t-butylthiophenol and 8 g. (0.1 mole) of 50% sodium hydroxide in 100 ml. of ethanol was added 34.3 g. (0.1 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide. The solution was heated at reflux for 30 minutes. It was then poured into 300 ml. of water and the organic product was extracted with ether. The ether extract was washed with water, dried over anhyd. Na_2SO_4, and evaporated down to a liquid residue which slowly crystallized. The yield of 2-t-butyl-4-methyl-6-(p-t-butylphenylthiomethyl)phenol was 31.6 g. (93%), m.p. 49—50° C. after recrystallization from hexane.

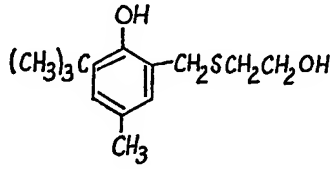
Analysis: Calc'd: — % C, 77.2;
% H, 8.85;
% S, 9.38.
Found: — % C, 77.0;
% H, 8.97;
% S, 9.35.

EXAMPLE No. 42.

Preparation of 2-t-butyl-4-methyl-6-(betahydroxyethylthiomethyl)phenol.

To a mixture of 686 g. (2 moles) of 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide and 156 g. (2 moles) of beta-mercaptoethanol in 700 ml. of ethanol was added 160 g. (2 moles) of 50% sodium hydroxide. The solution was heated at reflux for one hour and was then poured into 4 liters of cold water. The organic product was extracted with hexane-ether, washed with water, and dried over anhydrous sodium sulfate. The solvent was then removed by evaporation on the steam bath, leaving a liquid residue. The yield of 2-t-butyl-4-methyl-6-(beta-hydroxy-ethylthiomethyl)-phenol obtained was 502 g. (99%).

Formula:

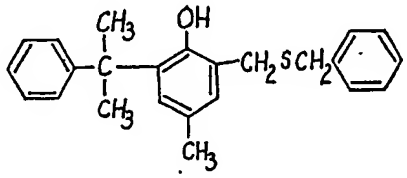


EXAMPLE No. 43.

Preparation of 2-(alpha,alpha-dimethylbenzyl)-4-methyl-6-(benzylthiomethyl)-phenol.

To a solution of 6.2 g. (0.05 mole) of benzyl mercaptan and 4 g. (0.05 mole) of 50% sodium hydroxide in 50 ml. of ethanol was added 20.2 g. (0.05 mole) of 2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl 2-benzothiazolyl sulfide. The solution was heated at reflux for 30 minutes. It was then poured into water and the product was extracted with hexane. The hexane extract was washed with water, dried over anhydrous sodium sulfate and evaporated down on the steam bath. 2-(alpha,-alpha-Dimethylbenzyl)-4-methyl-6-(benzylthiomethyl)phenol was isolated as a viscous oil, wt. = 15 g. (84%).

Formula:



In a similar manner, the following chemicals, for example, may be prepared: 2,4 - dimethyl - 6 - (methylthiomethyl)phenol, 2,4 - dimethyl - 6 - (dodecylthiomethyl)phenol, 2,4 - di - t - butyl - 6 - (cyclohexylthiomethyl)phenol, 2 - (dodecylthiomethyl) - 4 - methyl - 6 - (alpha - methylbenzyl)pheonl, 2 - (beta - hydroxyethylthiomethyl) - 4 - methyl - 6 - (alpha,alpha - dimethylbenzyl)phenol, 2 - (cyclohexylthiomethyl) - 4 - methyl - 6 - (alpha,alpha - dimethylbenzyl)phenol, 2 - (phenylthiomethyl) - 4,6 - di - (alpha - methylbenzyl)phenol, 2 - (ethylthiomethyl) - 4-methyl - 6 - cyclohexylphenol, 2,4 - di - t - butyl - 6 - (benzylthiomethyl)phenol, 2,4 - dicyclohexyl - 6 - (p - nonylphenylthiomethyl)phenol, 2 - dodecyl - 4 - methyl-6 - (benzylthiomethyl)phenol, and 2 - methyl - 4 - cyclooctyl - 6 - (octadecylthiomethyl)phenol.

EXAMPLE NO. 44.

The preparation of 2-t-butyl-4-methyl-6-(betahydroxy-ethoxymethyl) phenol.

2-Hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide (32.2 g., 0.098 mole) was suspended in 200 ml. of ethylene glycol (in this case the ethylene glycol is both the R"OH reactant described above and the solvent carrier for the reaction) and a solution of 6.6 g. (0.1 mole) of 85% potassium hydroxide in 10 ml. of water was added. The mixture was stirred and heated at 70—80° C. for four hours. Solution was almost complete. The mixture was filtered and the filtrate was diluted with water. Cloudiness was followed by separation of an oil which then crystallized. The product was extracted with hexane and the hexane extract was evaporated to an oil which crystallized. The yield of 2-t-butyl-4-methyl-6-(betahydroxyethoxymethyl)phenol was 17 g. (78%), m.p. 52—54° C. after recrystallization from hexane.

Analysis: Calc'd — % C, 70.7; % H, 9.3.
Found — % C, 70.2; % H, 9.5.

EXAMPLE NO. 45.

The preparation of 2-t-butyl-4-methyl-6-(methoxymethyl) phenol.

A mixture of 34.3 g. (0.1 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl benzothiazolyl sulfide and 17 ml. (0.1 mole) of 6 N. NaOH in 100 ml. of methanol was heated on the steam bath for 45 minutes. The solution was then diluted with water and the product was extracted with hexane. The hexane layer was washed with water and dried over potassium carbonate. The solution was then filtered and evaporated on the steam bath to a liquid residue. The yield of 2-t-butyl-4-methyl-6-(methoxymethyl)-phenol was 19 g. (91%).

In a similar manner, the following representative chemicals may be prepared:

2,4-dimethyl-6-methoxymethyl phenol
2-methyl-4-t-butyl-6-methoxymethyl phenol
2-octyl-4-methyl-6-ethoxymethyl phenol
2-(alpha,alpha-dimethylbenzyl)-4-methyl-6-ethoxymethyl phenol
2-cyclohexyl-4-methyl-6-ethoxymethyl phenol
2-t-butyl-4-methyl-6-isopropoxymethyl phenol
2-t-butyl-4-methyl-6-butoxymethyl phenol
2-t-butyl-4-methyl-6-cyclohexyloxymethyl phenol
2-t-butyl-4-methyl-6-benzyloxymethyl phenol
2-t-butyl-4-methyl-6-dodecyloxymethyl phenol
2,4-di(alpha,alpha-dimethylbenzyl)-6-methoxymethyl phenol
2-dodecyl-4-methyl-6-methoxymethyl phenol
2,4-dicyclohexyl-6-methoxymethyl phenol

Preferred starting materials are those selected from the group consisting of 2-hydroxy-3,5-dialkylbenzylbenzothiazolyl sulfide, 2-hydroxy-3-aralkyl-5-alkylbenzylbenzothiazolyl sulfide, and 2-hydroxy-3,5-diaralkylbenzylbenzothiazolyl sulfide.

Preferred products are those selected from the group consisting of 2,4-dialkyl-6-alkoxymethyl phenols, 2,4-dialkyl-6-(hydroxyalkoxymethyl)phenols, 2-aralkyl-4-alkyl-6-alkoxymethyl phenols, and 2,4-diaralkyl-6-alkoxymethyl phenols.

EXAMPLE No. 46.

Preparation of 2,6-di-t-butyl-4-methoxymethylphenol

A solution of 17 g. (0.05 mole) of the 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate, and 8.3 ml. (0.05 mole) of 6 N. NaOH in 50 ml. of methanol was heated to reflux for ten minutes. The solution was then diluted with water and the solid precipitate was filtered off and dried. The yield of 2,6-di-t-butyl-4-methoxymethylphenol was 12.5 g. (substantially quantitative), m.p. 98—100° C.

EXAMPLE No. 47.

Preparation of 2-methyl-4-(methoxymethyl)-6-t-butylphenol.

A solution of 29.7 g. (0.1 mole) of 3-methyl-4-hydroxy-5-t-butylbenzyl N,N-diethyldithiocarbamate and 16.6 ml. (0.1 mole) of 6 N. NaOH in 100 ml. of methanol was heated to reflux and then diluted with 150 ml. of water and cooled. The oil which separated was extracted with hexane. The hexane solution was concentrated and cooled. The product which crystallized was filtered off and dried. The yield of 2-methyl-4-(methoxymethyl)-6-t-butyl-phenol was 15 g. (72%), m.p. 64° C.

Analysis: Calc'd: — % C, 75.0; % H, 9.72
Found: — % C, 74.84; % H, 9.82.

EXAMPLE No. 48.

Preparation of 2,6-di-t-butyl-4-ethoxymethylphenol.

A solution of 17 g. (0.05 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate and 8.3 ml. (0.05 mole) of 6 N. NaOH in 50 ml. of ethanol was heated to reflux for five minutes. The solution was then poured into 100 ml. of cold water. The oil which separated was extracted with hexane. The hexane solution was washed with water, dried with anhyd. Na_2CO_3 and concentrated down. The 2,6-di-t-butyl-4-ethoxymethylphenol was obtained as a crystalline product, m.pt. 46° C., by cooling of the hexane solution and filtration.

Analysis: Calc'd: — % C, 77.3; % H, 10.60.
Found: — % C, 77.9; % H, 10.43.

EXAMPLE No. 49.

Preparation of 2,6-di-t-butyl-4-isopropoxymethylphenol.

A solution of 34 g. (0.1 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate and 16.6 ml. (0.05 mole) of 6N. sodium hydroxide in 60 ml. of isopropyl alcohol was allowed to stand at room temperature for 24 hours. The solution was then poured into 150 ml. of cold water. The oil which separated was extracted with hexane and the hexane extract was evaporated down to yield 2,6-di-t-butyl-4-isopropoxymethyl phenol, m.p. 59—60° C. after recrystallization from hexane.

EXAMPLE No. 50.

Preparation of 2-t-butyl-4-methyl-6-methoxymethylphenol.

A solution of 14.9 g. (0.05 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl N,N-dimethyldithiocarbamate and 4 g. (0.05 mole) of 50% sodium hydroxide in 50 ml. of methanol was heated at reflux for 30 minutes. The solution was then poured into 150 ml. of ice water. The organic product was extracted with hexane, washed with water and dried with anhydrous potassium carbonate. The solution was then evaporated down to yield 2-t-butyl-4-methyl-6-methoxymethylphenol as an amber oil weighing 9.3 g. (90% yield)

EXAMPLE No. 51.

Preparation of N-(2-hydroxy-3-t-butyl-5-methylbenzyl)-aniline.

To a solution of 4.7 g. (0.05 mole) of aniline and 9 ml. (0.05 mole) of 6N. NaOH in 50 ml. of ethanol was added 17.1 g. (0.05 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide. The solution was heated at reflux for 15 minutes. On cooling, the product crystallized out and was filtered off and dried. The yield of N-(2-hydroxy-3-t-butyl-5-methylbenzyl)aniline was 10 g. (74%), m.p. 118—121° C.

Analysis — Calc'd: % C, 80.4; % H, 8.62; % N, 5.21.
Found: % C, 80.4; % H, 8.72; % N, 5.64.

EXAMPLE No. 52.

Preparation of N,N-bis(2-Hydroxy-3-t-butyl-5-methylbenzyl)-hydroxylamine.

A solution of 34.3 g. (0.1 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl 2-benzothiazolyl sulfide, 3.5 g. (0.05 mole) of hydroxylamine hydrochloride and 27 ml. (0.15 mole) of 6N. sodium hydroxide in 75 ml. of ethylene glycol dimethyl ether was heated at reflux for 10 minutes. A white precipitate formed. The mixture was poured into water and the solid product was filtered off, washed with water and dried. The yield of N,N-bis(2-hydroxy-3-t-butyl-5-methylbenzyl)hydroxylamine was 17.5 g. (90%), m.p. 250° C. (dec.).

EXAMPLE No. 53.

Preparation of 2-(alpha,alpha-dimethylbenzyl)-4-methyl-6-(dimethylaminomethyl)phenol.

To a solution of 112 g. (0.6 mole) of 25% aqueous dimethylamine and 16 g. (0.2 mole) of 50% sodium hydroxide in 350 ml. of ethanol and 100 ml. of ethylene glycol dimethyl ether was added 81 g. (0.2 mole) of 2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl 2-benzothiazolyl sulfide. The mixture was heated at reflux for 30 minutes. The resulting solution was then cooled and the solid which precipitated out was filtered off, washed with ethanol and dried. The yield of 2-(alpha,-alpha-dimethylbenzyl)-4-methyl-6-(dimethylaminomethyl)phenol was 49 g. (87%), m.p. 106—107° C.

EXAMPLE No. 54.

Preparation of p-bis(3,5-di-t-butyl-4-hydroxybenzyl)-amino diphenylamine.

To a solution of 9.2 g. (0.05 mole) of p-aminodiphenylamine and 17.5 ml. (0.1 mole) of 6N. sodium hydroxide in 175 ml. of ethanol was added 34 g. (0.1 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate. The solution was heated at reflux for 10 minutes, a precipitate forming. The mixture was cooled and the product was filtered off, washed with ethanol and dried. The yield of p-bis(3,5-di-t-butyl-4-hydroxybenzyl)amino diphenylamine was 22 g. (71%), m.p. 201—203° C.

Analysis — Calc'd: % N, 4.51.
Found: % N, 4.40.

EXAMPLE No. 55.

Preparation of N,N-bis(3,5-di-t-butyl-4-hydroxy-benzyl)-β-naphthylamine.

To a solution of 7.1 g. (0.05 mole) of β-naphthylamine and 17.5 ml. (0.1 mole) of 6 N. NaOH in 250 ml. of ethanol was added 34 g. (0.1 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate. The mixture was heated at reflux for 10 minutes, a precipitate forming. The mixture was cooled and the product was filtered off, washed with ethanol and dried. The yield of N,N-bis(3,5-di-t-butyl-4-hydroxybenzyl)-β-naphthylamine was 19 g. (65%), m.p. 191—192° C.

Analysis — Calc'd: % N, 2.42.
Found: % N, 2.48.

EXAMPLE No. 56.

Preparation of N,N-bis(3-methyl-4-hydroxy-5-t-butylbenzyl)-hydroxylamine.

To a solution of 3.5 g. (0.05 mole) of hydroxylamine hydrochloride and 27 ml. (0.15 mole) of 6N. sodium hydroxide in 100 ml. of ethanol was added 30 g. (0.1 mole) of 3-methyl-4-hydroxy-5-t-butylbenzyl N,N-dimethyldithiocarbamate. The mixture was heated at reflux for 15 minutes, a precipitate forming. The mixture was diluted with 200 ml. of water and the product was filtered off and dried. The yield of N,N-bis(3-methyl-4-hydroxy-5-t-butylbenzyl) hydroxylamine was 18.5 g. (96%), m.p. 218—220° C. after recrystallization from ethanol.

EXAMPLE No. 57.

Preparation of N-methyl-N-(2-hydroxy-3-t-butyl-5-methyl-benzyl)aniline.

To a solution of 10.7 g. (0.1 mole) of N-methylaniline and 8 g. (0.1 mole) of 50% sodium hydroxide in 50 ml. of ethanol was added 29.7 g. (0.1 mole) of 2-hydroxy-3-t-butyl-5-methylbenzyl N,N-dimethyldithiocarbamate. The solution was heated at reflux for 30 minutes. On cooling, the product precipitated out. The mixture was diluted with a small amount of water, added dropwise, to aid separation of the product. The product was then filtered off, washed with aqueous ethanol and dried. The yield of N-methyl-N-(2-hydroxy-3-t-butyl-5-methylbenzyl)aniline was 24 g. (85%), m.p. 67—68° C.

EXAMPLE No. 58.

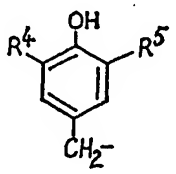
Preparation of N-methyl-N-(2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl)aniline.

To a solution of 5.4 g. (0.05 mole) of N-methylaniline and 4 g. (0.05 mole) of 50% sodium hydroxide in 50 ml. of ethanol was added 18 g. (0.05 mole) of 2-hydroxy - 3 - (alpha,alpha - dimethyl - benzyl) - 5 - methylbenzyl N,N - dimethyldithiocarbamate (prepared in 47% yield from reaction of the corresponding Mannich base with carbon disulfide). The mixture was heated at reflux for 30 minutes. The resulting solution was poured into water and extracted with hexane. The hexane extract was washed with water, dried over anhydrous sodium sulfate and evaporated down to a viscous liquid residue. The yield of N-methyl-N-(2-hydroxy-3-(alpha,alpha-dimethylbenzyl)-5-methylbenzyl)-aniline was 17 g. (98%).

WHAT WE CLAIM IS:—

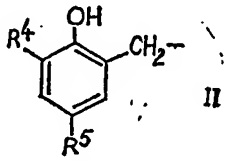
1. A method of making a compound of the formula A_2S, AOR, ASR^1, A_2NR^2, ANR^2R^3 or A—S—X—S—A; wherein:—

A represents



I

or



II

R^4 and R^5 being the same or different and representing alkyl, cycloalkyl or aralkyl groups having up to 12 carbon atoms,

R represents an alkyl, cycloalkyl, aralkyl or hydroxyalkyl group having up to 12 carbon atoms,

R^1 represents an alkyl, hydroxyalkyl, aryl, cycloalkyl or aralkyl group having up to 18 carbon atoms,

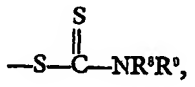
R^2 and R^3 may be the same or different and represent H, OH or an alkyl, cycloalkyl, hydroxyalkyl, aralkyl or aryl group having up to 12 carbon atoms, or NR^6R^7, R^6 and R^7 being the same or different and representing hydrogen or alkyl, cycloalkyl, aralkyl or aryl groups having up to 12 carbon atoms,

and X represents a diradical containing from 2 to 18 carbon atoms;

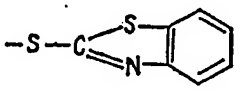
which method comprises treating a compound having the formula AZ, wherein

A has the above significance, and

Z represents



R^8 and R^9 being the same or different and representing lower alkyl groups (as herein defined), or, in the case where A has formula II above, Z may alternatively represent



with an alkali metal sulfide, or with an alkali metal hydroxide and an active hydrogen containing compound having the formula ROH, R^1SH, NH_2R^2 or NHR^2A, NHR^2R^3 or H—S—X—S—H, wherein

R, R^1, R^2, A and R^3 and X have the above significance, the reaction being effected in an inert solvent, or when ROH is used, in an excess of ROH, and isolating the resulting compound of the formula A_2, AOR, ASR^1, A_2NR^2, ANR^2R^3 or A—S—X—S—A.

2. A method as claimed in Claim 1, wherein the solvent is a water miscible solvent or a mixture of an aromatic hydrocarbon and water.

3. A method as claimed in Claim 2, wherein the solvent is acetone, an aliphatic alcohol, dioxan, ethylene glycol dimethyl ether or a mixture of water with benzene or xylene.

4. A method as claimed in Claims 1, 2 or 3, which is effected at a temperature between 20°C. and 100°C.

5. A method as claimed in Claim 4, which is effected at a temperature between 50°C. and 100°C.

6. A method as claimed in Claims 4 or 5 which is effected under reflux.

7. A method as claimed in any one of the preceding claims, wherein the alkali metal sulfide or hydroxide is a sodium or potassium sulfide or hydroxide.

8. A method as claimed in any one of the preceding claims wherein one mole of the alkali metal sulfide is reacted with two moles of the compound AZ.

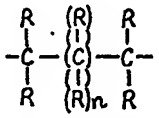
9. A method as claimed in Claim 8, wherein Group A in the compound AZ, has the formula I wherein R^4 is methyl and R^5 is tert. butyl.

10. A method of making A—S—X—S—A as claimed in any one of Claims 1 to 9, wherein one mole of the compound H—S—X—S—H is reacted with 2 moles of the compound AZ.

11. A method as claimed in Claim 10, wherein X represents:—

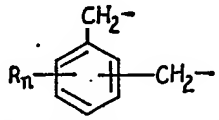
(a) $-(CH_2)_n-$ wherein n is an integer from 2 to 12,

(b)



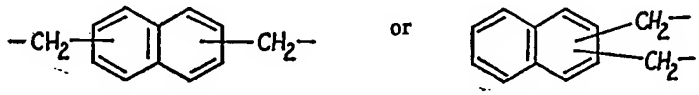
wherein R represents a hydrogen atom or an alkyl group, at least one R representing an alkyl group, and n is an integer from 0 to 9,

(c)



wherein R is an alkyl group having from 1 to 4 carbon atoms and n is an integer from 0 to 4

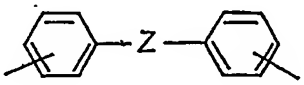
(d)



(e)

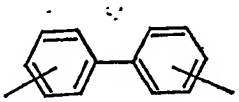
wherein R is an alkyl radical and n is an integer from 0 to 4

(f)

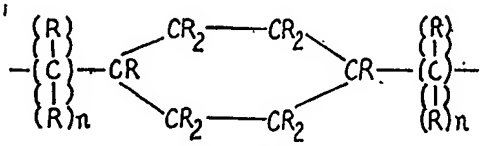


wherein Z represents O, S, or SO_2.

(g)

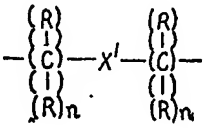


(h)



wherein R represents hydrogen or an alkyl group and n is an integer from 0 to 6

(i)



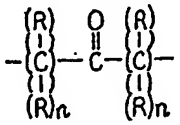
wherein R represents hydrogen or an alkyl group, n is an integer from 1 to 6 and X^1 represents O, S, SO_2 or NR^1 wherein R^1 represents an alkyl group.

(j)

$-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-$ or

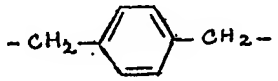
$CH_2-CH_2-O-CH_2-O-CH_2-CH_2-$, or

(k)



wherein R represents hydrogen or an alkyl group and n is an integer from 1 to 5.

12. A method as claimed in Claim 11, wherein, in the compound AZ, R^4 and R^5 in formulae I or II represent methyl or tert. butyl groups, and, in the compund H—S—X—S—H, X represents $-CH_2-CH_2-$,



or $-CH_2-CH_2-O-CH_2-CH_2-$.

13. A method of making ASR^1 as claimed in any one of Claims 1 to 9, wherein one mole of R^1SH is reacted with one mole of the compound AZ in the presence of one mole of the alkali metal hydroxide.

14. A method as claimed in Claim 13, wherein R^1 represents $-CH_2-CH_2-OH$, $-CH_2-Ar$ or Ar, wherein Ar represents any aryl group.

15. A method as claimed in Claim 14, wherein R^1 is a p-tert. butyl-phenyl group.

16. A method of making AOR as claimed in any one of Claims 1 to 9 wherein one mole of alkali metal hydroxide and at least one mole of ROH are reacted with one mole of AZ.

17. A method as claimed in Claim 16, wherein R, in ROH, represents methyl or β-hydroxy-ethyl.

18. A method as claimed in any one of Claims 10 to 17 wherein, in the radical A, R^4 and R^5 represent methyl or tert.butyl groups.

19. A method of making A_2NR^2 as claimed in any one of Claims 1 to 9, which comprises reacting one mole of AZ with one mole of the alkali metal hydroxide and either one mole of $ANHR^2$ or 1/2 mole of R^2NH_2.

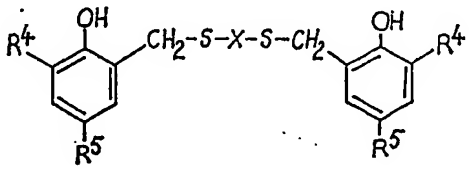
20. A method of making ANR^2R^3 as claimed in any one of Claims 1 to 9, which comprises reacting one mole of AZ with one mole of the alkali metal hydroxide and one mole of R^2R^3NH.

21. A method as claimed in Claims 19 or 20, wherein R^4 and R^5 in the radical A represent methyl, tert.butyl or alpha,alpha-dimethyl benzyl groups.

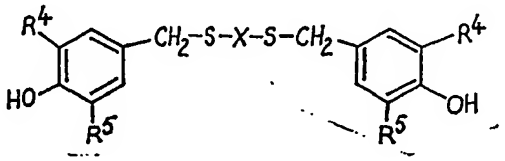
22. A method as claimed in Claims 19, 20 or 21 wherein NH_2R^2 or NHR^2R^3 is hydroxylamine, dimethylamine, p-phenylene diamine, β-naphthylamine, aniline or N-methyl aniline.

23. A method as claimed in Claim 1, substantially as described in any one of the foregoing Examples excepting Example 17.

24. A compound having the formula



or

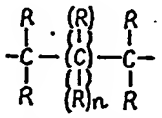


wherein R^4 and R^5 may be the same or different and represent alkyl, cycloalkyl or aralkyl groups having up to 12 carbon atoms and X is a diradical containing from 2 to 18 carbon atoms.

25. A compound as claimed in Claim 24 wherein X represents:—

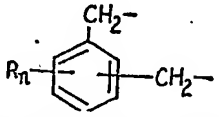
(a) $-(CH_2)_n-$ wherein n is an integer from 2 to 12,

(b)



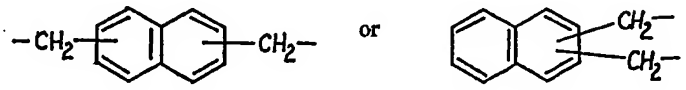
wherein R represents a hydrogen atom or an alkyl group, at least one R representing an alkyl group, and n is an integer from 0 to 9,

(c)

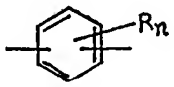


wherein R is an alkyl group having from 1 to 4 carbon atoms and n is an integer from 0 to 4

(d)

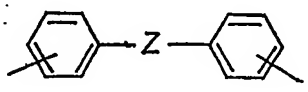


(e)



wherein R is an alkyl radical and n is an integer from 0 to 4

(f)



wherein Z represents O, S or SO_2.

50. Beta,beta'-bis(2-hydroxy-3-nonyl-5-methylbenzylthio)-diethyl ether.
51. A bis(2-hydroxy-3-aralkyl-5-alkylbenzylthio)alkylbenzene.
52. Alpha,alpha' - bis(2 - hydroxy - 3 - (alpha,alpha' - dimethylbenzyl) - 5-methylbenzylthio)-p-xylene.
53. A bis(2-hydroxy-3-alkyl-5-alkylbenzylthio)-diphenyl ether.
54. p,p'-Bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)diphenyl ether.
55. A bis(2-hydroxy-3-alkyl-5-alkylbenzylthio)alkyl cyclohexane.
56. Beta(2 - hydroxy - 3 - t - butyl - 5 - methylbenzylthio) - ethyl - 4 - (2-hydroxy - 3 - t - butyl - 5 - methylbenzylthio)cyclohexane.
57. A bis(2-hydroxy-3-alkyl-5-alkylbenzylthio)diethyl sulfide.
58. Beta,beta'-bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)diethyl sulfide.
59. A bis(2-hydroxy-3-alkyl-5-alkylbenzylthio)biphenyl.
60. p,p'-Bis(2-hydroxy-3-t-butyl-5-methylbenzylthio)biphenyl.

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